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A. Tamimi[a]; O. F. Abdel-salam[a]
[a] CHEMICAL ENGINEERING DEPARTMENT, COLLEGE OF ENGINEERING JORDAN UNIVERSITY OF SCIENCE & TECHNOLOGY, IRBID, JORDAN

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# Washing the Extraction of El-lajjun Oil-Shale Deposits with a Mixture of Organic Solvents

A. TAMIMI and O. F. ABDEL-SALAM
CHEMICAL ENGINEERING DEPARTMENT
COLLEGE OF ENGINEERING
JORDAN UNIVERSITY OF SCIENCE & TECHNOLOGY
IRBID, JORDAN



## Abstract

El-lajjun oil-shale deposits were extracted with organic solvents. Appreciable amounts of oil were extracted. The recovery may reach up to 75% in the three contacting stages of a CSTR-type extractor.

## INTRODUCTION

Most processes utilizing oil shale involve direct combustion or retorting. The use of organic solvents to extract the oil from shale is quite new in the field, although solvent–solid extraction by itself as a unit operation is an old technique. The field may be subdivided into three main categories: leaching, washing extraction, and diffusional extraction.

Leaching involves the contacting of a liquid and a solid and the imposing of a chemical-physical interaction upon one or more solute components in the solid matrix so as to render them soluble. In washing extraction the solid is crushed to a certain size, permitting the solute constituents to be washed from the matrix. In diffusional extraction the soluble product diffuses across the solid pores and is washed out from the solid surface to the bulk of the solvent. Oil-shale extraction falls under washing extraction since it is assumed to be a simple physical dissolution process.

The distribution of oil inside the shale is uneven. In certain areas it was found as a heterogeneous complex of oil and shale, and sometimes it is found in small amounts between the shale layers. In other localities it is found as scattered isolated pockets, and sometimes the oil is accumulated in small cracks.

The organic material in oil shale is called kerogen. It is a heterogeneous structure of "organic minerals." Oil-shale petrographers have identified various minerals and hydrocarbon constituents. Analysis indicated that it consists primarily of carbon, hydrogen, oxygen, nitrogen, and sulfur. Also, trace quantities of other elements are found (*1*). The linkage between kerogen and its host shale is an area of considerable debate and needs further research.

The extent of extracting oil from shale is determined by the base of soluble oil present in the shale (asphaltene base, naphthenic base, or paraffinic base), its distribution throughout the solid, particle size and porosity of the shale, pore size distribution, nature of bonds between the oil and the shale, the physical properties of the chemical solvent used (viscosity, surface tension, adhesiveness, solubility, volatility, flammability) and the operating conditions (temperature, pressure, contact time, rate of agitation during extraction, and solvent to oil-shale ratio) (*2–4*).



## SYSTEM DESCRIPTION

Oil shale was crushed and screened into several ranges of particle size (0.1–2 mm). Each batch of a specific particle size was processed into an extractor. The extractor is a cylindrical vessel with a conical false bottom packed with steel wool, and it is supplied with a regulating valve at the outlet line. The crushed oil-shale batches were dumped into the extractor to a certain depth.

Various organic solvents, such as toluene, benzene, cyclohexane, pentane, ethylether, and ethylbenzene, were tested. A mixture of 75% benzene and 25% cyclohexane was found to be the best solvent to produce high yields of extracted oil.

The solvent mixture was heated up to certain operating temperature and poured into the extractor. The batch was mixed thoroughly to permit exposure of all particles to the solvent and to increase the rate of extraction. At end of the experiment the extract was allowed to percolate and flow through the bed of crushed oil under gravity, where it was filtered by the packed steel wool, and then collected and separated into solvents and oil by means of a rotary evaporator. The organic solvent mixture was further distilled and recycled again for use as a fresh solvent. The batch experiment assembly is shown in Fig. 1.

In actual operation it is impossible to completely separate the liquid phase (extract) from the solid. Some solution will adhere to the solid surface and fill the spaces between the particles. The amount of solution retained by or adhering to the particles of any batch was determined experimentally by the difference in weight between the fresh solid batch and the extracted batch. It was found to be almost constant, but it did vary slightly with

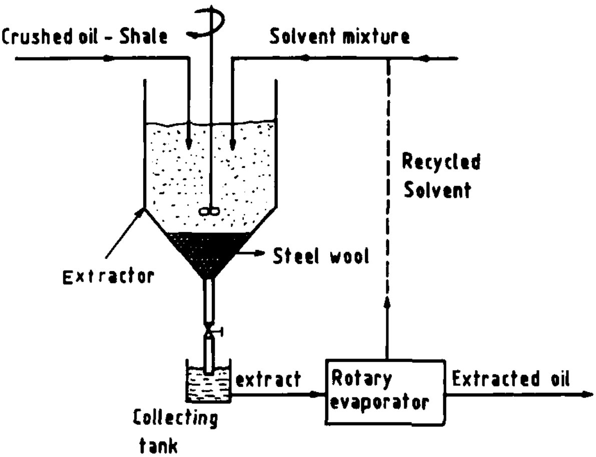


FIG. 1. Batch extraction of oil shale by organic solvents.



particle size and the mass fraction of solute in the solution. The smaller the particle size, the higher the value of retained solution within the solid. The average value of this solution retained in the various particle sizes used in this study was 200 g/1 kg solids.

## ANALYSIS AND MODELING

The system may be considered to consist of three main constituents:

1. The organic solvent mixture: designated by S.
2. The solute (kerogen): designated by A.
3. The inert solids (shale): designated by I.

For the purpose of theoretical analysis, the kerogen is considered to be a single substance which dissolves infinitely in the solvents, even though it is a mixture of several constituents. Similarly, the solids (shale) are treated as a single insoluble material that is not entrained in the solvent.

We now define the following:

$Y_A$: Kerogen (solute concentration in the extract on a solid-free basis, i.e., $\left(\dfrac{\text{solute}}{\text{solvent} + \text{solute}}\right)$

$X_A$: Kerogen (solute) concentration in the solution adhering to the solids on a solid-free basis, i.e., $\left(\frac{\text{solute}}{\text{solvent + solute}}\right)$

$Y_I$: Solids (shale) concentration on a solid-free basis, i.e., $\left(\frac{\text{inerts}}{\text{solvent + solute}}\right)$

$y_S$: Mass fraction solvent, i.e., $\left(\frac{\text{solvent}}{\text{solvent + solute + solids}}\right)$

$x_A$: Mass fraction solute, i.e., $\left(\frac{\text{solute}}{\text{solvent + solute + solids}}\right)$



In leaching, the ideal stage concept requires that the solution in the extract and the one adhering to the solids have the same composition (*5*). Also, for insoluble solids (shale) under complete drainage with no entrainment, the solid concentration in the extract is zero, that is, $Y_I = 0.0$.

For El-lajjun oil shale, the soluble hydrocarbon content is about 12.0% on a weight basis according to data published by Natural Resources Authority of Jordan (*1*). This was verified experimentally by the difference in weight before and after complete devolatilization of several samples at high temperatures.

Now consider a single contact stage as shown in Fig. 2. $L_0$ kilograms of fresh crushed oil shale with composition $X_A$ of oil content is charged to

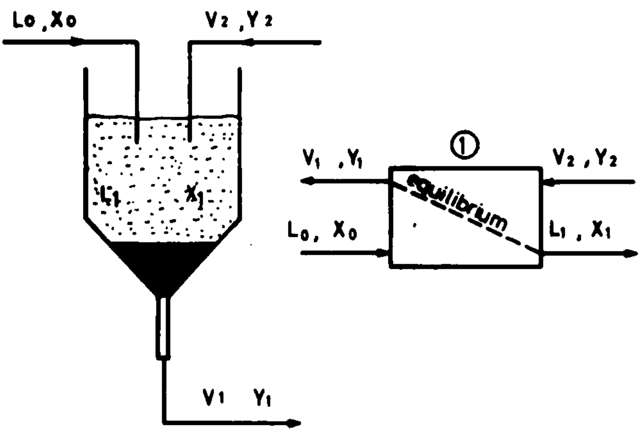


FIG. 2. Modeling of the first stage.

the extractor where it is brought into contact with $V_2$ kilograms of a solvents mixture. The extract stream has $V_1$ kilograms with $Y_{A1}$ composition of solute (kerogen) on a solid-free basis. Making a mass balance around stage number 1 yields

$$\text{Total mass balance: } L_0 + V_2 = V_1 + L_1 \tag{1}$$

$$\text{Solute mass balance: } L_0 x_{A0} = V_1 y_{A1} + L_1 x_{A1} \tag{2}$$

If we denote the total weight of the mixture in the stage (solvents + oil shale) by $m$ kilograms and its composition by $x_m$, then

$$m = L_0 + V_2 \tag{3}$$

The lever rule can be applied, making an oil (solute) balance:

$$m x_{Am} = L_0 x_{A0} + V_2 y_{A2} \tag{4}$$

Substituting Eq. (3) into Eq. (4) and re-arranging yields

$$\frac{V_2}{L_0} = \frac{x_m - x_{A0}}{y_{A2} - x_{Am}} \tag{5}$$

$V_2/L_0$ is the solvent/oil-shale ratio used in the contact stage. Various ratios were tried, but the economics of the process control the selected value. In this study, 0.5 kg solvents mixture was used per 1 kg oil shale fed to the extractor. Graphically, the process is presented on a right-triangle diagram in Fig. 3.

For multiple-contacting stages, the model is presented in Fig. 4. The overall analysis follows the same steps as for a single stage (*6*).

## RESULTS AND DISCUSSION

Calculations of the oil-shale washing extraction system are based only on the materials balance and the concept of an ideal stage. Graphically, this can be done on a right-triangle diagram at constant operating conditions (temperature, particle size, mixing rate, extraction time, and solid/solvent ratio).

The horizontal axis represents the locus of all possible oil contents in oil shale on a solvent-free basis. This axis is designated by $x_A$. Similarly, the vertical axis represents the locus of all possible mixtures of solvent and insoluble solids (shale) on a solute-free basis, and it is designated by $y_S$.

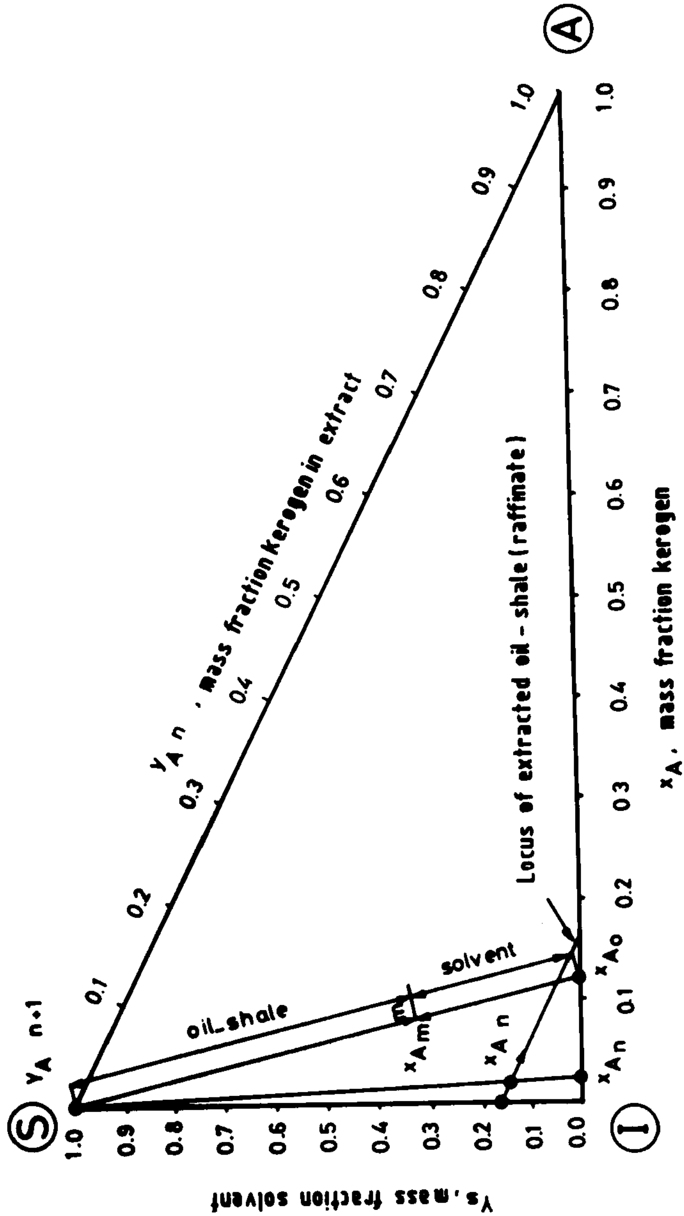


FIG. 3. Right-triangle diagram of oil-shale extraction.

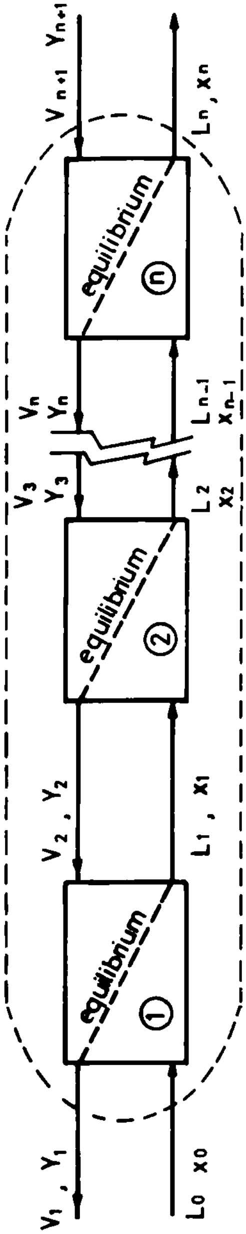


FIG. 4. Presentation of multiple countercurrent stages.

The hypotenuse of the triangle represents the locus of all possible compositions of the extract on a solid-free basis. Any point inside the triangle represents a mixture of all three constituents. The origin represents the solids, that is, $x_A = y_S = 0.0$.

Data are given as $y$–$x$ mass fractions on the right-triangle diagram, with no solubility or entrainment of the shale in the liquid extract and with constant solution retainment in the raffinate shale. Thus, the locus of the extracted solids is a line parallel to the hypotenuse which intersects the vertical axis at

$$y_S = \frac{\text{kg retained solution/kg solids}}{1 + \text{kg retained solution/kg solids}}$$

Then

$$y_S = \frac{0.200}{1 + 0.200} = 0.167$$

Every kilogram of El-lajjun oil shale contains 120 g oil, that is, 12% on a weight basis. Economically, it is not feasible to extract all the oil from the shale. In this study the oil left in the raffinate shale was up to 2% on a weight basis, that is, $x_n = 0.02$.

The overall mass balance on the $n$ stages of Fig. 4 yields

$$L_0 + V_{n+1} = L_n + V_1 = m$$

The kerogen mass balance is

$$L_0 x_{A0} + V_{n+1} Y_{A\ n+1} = L_n x_{An} + V_1 y_{A1} = m x_{Am}$$

The points $x_{A0}$, $y_{A\,n+1}$ and $x_{An}$ are located on the diagram from the given data of the process as shown in Fig. 3. The points $x_{Am}$, $Y_{A\ n+1}$, and $x_{A0}$ must lie on the same straight line where $x_{Am}$ divides the distance between $x_{A0}$ and $y_{A\ n+1}$ in the ratio of kilograms solvent used/kilogram oil shale. That is:

$$\frac{v_{n+1}}{L_0} = \frac{0.5 \text{ kg solvent}}{1 \text{ kg oil shale}}$$

The point $m$ is the sum of $L_n$ and $V_1$. Thus, the points $x_{An}$, $x_{Am}$, and $y_{A1}$ must lie on one straight line. Accordingly, $y_{A1}$ is located by extrapolating the straight line that passes through the points $x_{An}$ and $x_{Am}$ to meet the locus of the etract (i.e., the hypotenuse).

For these operating conditions, two theoretical stages were sufficient. This is illustrated graphically in Fig. 5.

In fact, we need more stages. This depends on extraction efficiency. One more stage is usually used to substitute for deviation from the ideal stage concept. The recovery calculation was based on the amount of oil extracted

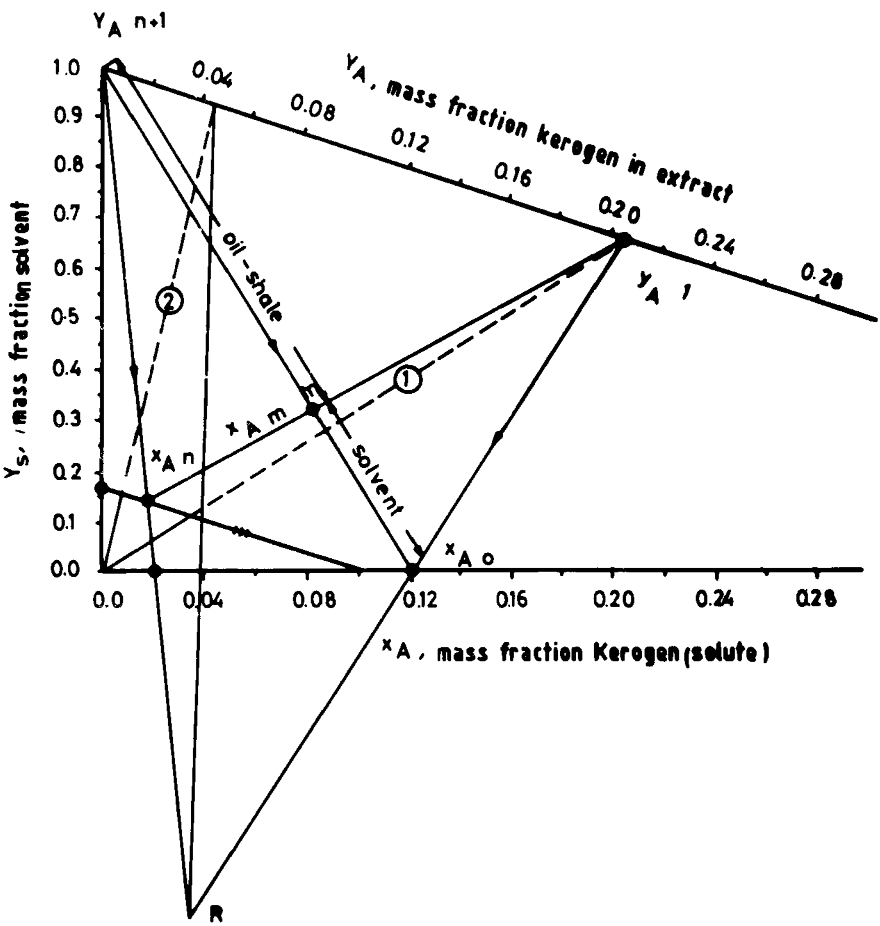


FIG. 5. Number of theoretical stages required for oil-shale extraction.

per kilogram of oil shale fed to the extractor. That is:

$$\text{Recovery }\% = \frac{V_1 Y_{A1}}{L_0 X_{A0}} \times 100 = \frac{0.4 \times 0.22}{1 \times 0.12} = 73.3$$

## CONCLUSION

Extracting oil from oil shale by organic solvents is quite new in the field, and seems to be a potential process to utilize oil shale. The process is still in its preliminary stages and needs more research. Appreciable amounts of oil were extracted by certain types of organic solvents. The selection of the organic solvent, the operating conditions, and the proper particle size are the key factors in this process. Kerogen, which is the desired product to be extracted, is composed of a wide spectrum of hydrocarbons. Those include paraffinic, naphthenic, aromatic, and asphaltene compounds. Thus, the use of a single solvent is not efficient, but a mixture of certain selected solvents is more practical. In this study a mixture of 75% benzene and 25% cyclohexane was used. These two compounds have almost identical boiling points (= 80°C). Thus, they can be separated easily from the extract in one step by a rotary evaporator in a normal water bath.

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